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between the ipso-carbons of the mesityl rings and the Al atom show two which are approximately 120° and one which is much smaller, 108.6° . Again, C19 is the ipso-carbon atom (ring C) that is unique.

These observations and inspection of Figure 1 provide a qualitative explanation for this structural arrangement. Ring A is at the furthest position from the THF molecule; ring B is oriented so that the ortho-methyl group closest to the THF molecule is pointed away from it. Ring C lies nearly under the THF molecule and is twisted such that it is almost coplanar with respect to the plane of the ipso-carbon atoms, thus minimizing the steric interactions with the THF molecule.

The geometry is further modified by the steric repulsion of the ortho methyl groups of the mesityl rings. These groups on ring C then force the angle between itself and rings A and B to be larger than expected for an ether adduct of a triorganoaluminum while the angle between these latter two rings is smaller than expected. Likewise, the rings are oriented such that the steric repulsions between the ortho methyl groups is minimized. This overall arrangement also provides a reasonable orientation for molecular packing.

It appears from this structure that considerable steric crowding exists in this molecule but that the energy gained by formation of the THF adduct, although probably less than optimal, is sufficient to yield a reasonably stable addition product. We are in the process of investigating the structure of other adducts of 1 to further explore this fine balance between steric and electronic effects in other sterically crowded organoaluminum complexes.

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Supplementary Material Available: Complete listings of bond lengths (Table S-I), bond angles (Table S-II), anisotropic thermal parameters (Table S-III), and hydrogen atom positional coordinates and isotropic thermal parameters (Table S-IV) and a packing diagram (Figure S-1) (7 pages); a listing of observed and calculated structure factors (Table S-V) (23 pages). Ordering information is given on any current masthead page.

C,C Couplings in the Reactions of Unsaturated Group 4 Metal *s-cis*-Butadiene Complexes with 2,6-Xylyl Isocyanide

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A group of electronically unsaturated (14-electron) diene complexes of Hf and Ti has been reacted with 2,6-xylyl isocyanide. $\text{Cp}^*\text{Hf}(\text{diene})\text{Cl}$ (diene = 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) reacts with 2 mol of isocyanide to form the unusual heterospiro complexes $\text{Cp}^*\text{Hf}(\text{Cl})\text{N}(\text{xy})\text{CCH}_2\text{C}(\text{Me})=\text{C}(\text{R})\text{CH}=\text{CHN}(\text{xy})$ (R = H, Me; xy = 2,6-xylyl) involving a 1,2-hydrogen shift and a ring closure after insertion of isocyanide into the Hf-diene bond. In $\text{Cp}^*\text{Hf}(2,3\text{-dimethyl-1,3-butadiene})\text{R}$ (R = Me, Ph, neopentyl) the size of R determines whether insertion into the Hf-R bond (R = Me) or the Hf-diene bond (R = Ph, neopentyl) takes place. $\text{Cp}^*\text{Ti}(2,3\text{-dimethyl-1,3-butadiene})\text{Cl}$ reacts through elimination of the diene ligand and C,C coupling of two isocyanides to form $(\text{Cp}^*\text{TiCl})_2[\mu\text{-N}_2\text{C}_2(\text{xy})_2]$. This compound crystallizes in space group $P2_1/c$ with $a = 11.111(8) \text{ \AA}$, $b = 19.435(17) \text{ \AA}$, $c = 8.592(4) \text{ \AA}$, $\beta = 109.68(5)^\circ$ at 170 K, $Z = 2$, and $d_{\text{calcd}} = 1.33 \text{ g cm}^{-3}$. The molecule is centered around an approximately planar raftlike $\text{Ti}_2\text{N}_2\text{C}_2$ structure with a bridging nonlinear $(\text{xy})\text{NCCN}(\text{xy})$ ligand. As side products two enediamide complexes deriving from double and triple insertion of isocyanide into the Ti-diene bond could be identified. The difference in reactivity between the Ti and Hf complexes demonstrates the decrease in σ^2, π -metallacyclopentene character in $\text{Cp}^*\text{M}(\text{diene})\text{Cl}$ going from M = Hf to M = Ti.

Introduction

Group 4 transition-metal compounds containing an *s-cis*-butadiene ligand have been shown to exhibit pronounced σ^2, π -metallacyclopentene character, both in the 18-electron $\text{Cp}_2\text{M}(\text{diene})$ (M = Zr, Hf)¹ and in the 14-

electron $\text{Cp}^*\text{M}(\text{diene})\text{Cl}$ (M = Ti, Zr, Hf; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)² system. This causes $\text{Cp}^*\text{M}(\text{diene})\text{Cl}$ to react with polar organic substrates like ketones,^{3a} nitriles,^{3b} and CO,⁴ as a

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(1) Extensive information on the $\text{Cp}_2\text{M}(\text{butadiene})$ (M = Zr, Hf) system can be found in: Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* 1985, 18, 120. Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* 1985, 24, 1 and references cited therein.

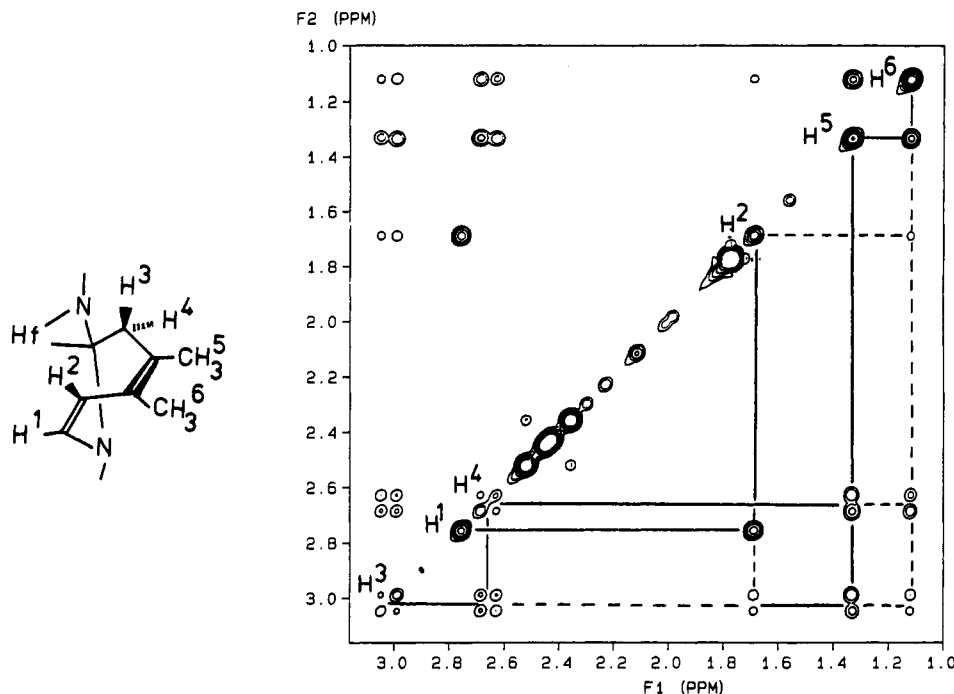


Figure 1. 2D ^1H , ^1H -COSY NMR spectrum of 3.

dialkyl complex, yielding products which derive from insertion of the organic molecule into the M-C σ -bonds. In contrast, with acetylenes diene elimination is observed in most cases.^{5a} This ambivalence in reactivity is one of the interesting aspects of these compounds. Reactions of transition-metal complexes with isocyanides have been much investigated also because they provide model systems for reactions with carbon monoxide. With group 4 alkyl and hydrido complexes reaction products have been found ranging from simple iminoacyls like $\text{Cp}_2\text{Zr}[\eta^2\text{-C(R)=N(R')}]X$ (R, R' = H, alkyl, aryl; X = Cl, Me)⁶ to considerably more complicated structures formed through consecutive insertions and C,C-coupling reactions.⁷ So far no isocyanide reactions of group 4 diene complexes have been published. Here we wish to report the reactions of $\text{Cp}^*\text{M}(\text{diene})\text{R}$ (M = Hf, diene = 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, R = Cl, Me, Ph, neopentyl; M = Ti, diene = 2,3-dimethyl-1,3-butadiene, R = Cl²) with 2,6-xylyl isocyanide. The ambivalent reactivity of the group 4 diene complexes is clearly expressed in the differences in product formation between the Ti and Hf compounds.

Results and Discussion

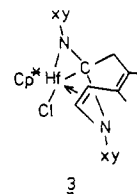
Reaction of $\text{Cp}^*\text{Hf}(\text{diene})\text{Cl}$ (Diene = 2,3-Dimethyl-1,3-butadiene (1), 2-Methyl-1,3-butadiene (2)) with 2,6-Xylyl Isocyanide. 1 reacts with 2 mol of 2,6-xylyl isocyanide in toluene at room temperature to form a white crystalline product of stoichiometry $\text{C}_{34}\text{H}_{43}\text{ClHfN}_2$ (elemental analysis), which is monomeric in benzene solution (cryoscopy). For this product we propose the

Table I. ^1H NMR Data of $\text{Cp}^*\text{Hf}(\text{Cl})\text{N}(\text{xy})\text{CCH}_2\text{C}(\text{Me})=\text{C}(\text{R})\text{CH}=\text{CHN}(\text{xy})^a$

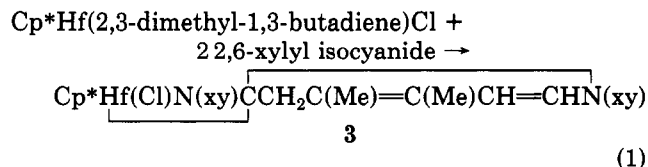
R	Cp*	Me	R	CH_2	$=\text{CH}$	xy-Me
Me (3)	1.78	1.12	1.33	2.67 (d, 17.0) 3.03 (d, 17.0)	1.70 2.77 (d, 2.3)	2.36 2.43 2.46 2.53
H (4)	1.78	1.41	4.70	2.59 (d, 17.8) 3.04 (d, 17.8)	1.67 2.77 (d, 2.2)	2.35 2.43 2.47 2.49

^a 300 MHz, C_6D_6 , 20 °C. Chemical shifts in ppm. Coupling constants in Hz in parentheses. Unresolved long-range couplings not given. Aromatic xylyl protons at 7.1–6.9 ppm (m).

structure $\text{Cp}^*\text{Hf}(\text{Cl})\text{N}(\text{xy})\text{CCH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}=\text{CHN}(\text{xy})$ (3, xy = 2,6-xylyl), a heterospiro compound



with a three-membered HfNC and a seven-membered C_6N ring joined together at one quaternary carbon atom, which could be considered as a Cp^*HfCl complex of a cyclic amidine (eq 1). Repeated attempts to obtain single



crystals suitable for X-ray analysis failed, but a combination of NMR and IR spectroscopy allows a good structure assignment. The ^1H NMR spectrum (Table I) shows a methylene group with two diastereotopic protons, two

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Table II. ^{13}C NMR Data of $\text{Cp}^*\text{Hf}(\text{X})\text{N}(\text{xy})\text{C}^1\text{C}^2\text{H}_2\text{C}^3(\text{C}^4\text{H}_3)=\text{C}^5(\text{R})\text{C}^6\text{H}=\text{C}^7\text{HN}(\text{xy})^a$

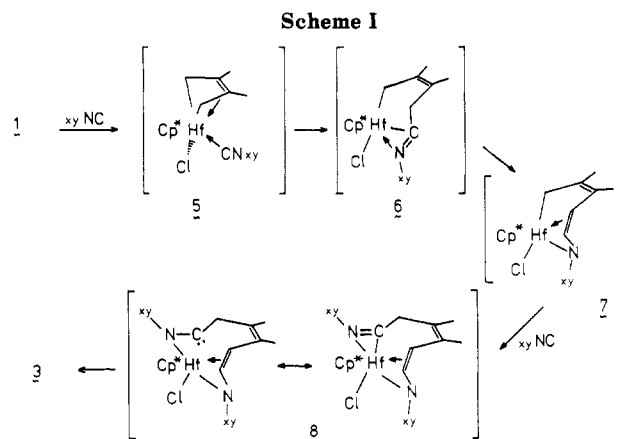
X, R	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ⁷	R	X
Cl, Me (3) ^b	44.71	41.76 (t, 129.8)	130.54	13.41 (q, 125.2)	<i>e</i>	28.66 (d, 168.5)	43.80 (d, 183.4)	12.82 (q, 125.5)	
Cl, H (4) ^b	47.37	36.88 (t, 131.1)	139.56	16.65 (q, 126.1)	120.89 (d, 163.4)	27.44 (d, 164.1)	43.56 (d, 183.9)		
Np, Me ^c	46.6	43.2 (t, 132)	<i>e</i>	13.6 (q, 127)	<i>e</i>	30.7 (d, 169)	44.0 (d, 185)	13.2 (q, 126)	α 73.2 (t, 102) β 38.0 γ 37.2 (q, 125) α 189.6, <i>f</i>
Ph, Me ^d	45.4	43.9 (t, 134)	<i>e</i>	13.4 (q, 127)	<i>e</i>	31.7 (d, 168)	43.8 (d, 180)	12.9 (q, 126)	

^a Chemical shifts in ppm. ¹ J_{CH} in Hz in parentheses. Xylyl resonances not given. C_5Me_5 and $\text{C}_6(\text{CH}_3)_5$ between 118.9 and 119.6 and 10.5 and 11.1 ppm, respectively. ^b 75.4 MHz, C_6D_6 , 20 °C. ^c 50.3 MHz, $\text{THF}-d_8$, 20 °C. ^d 50.3 MHz, C_6D_6 , 20 °C. ^e Not identified. ^f Ph CH resonances not assigned due to interference with xy-CH resonances.

nonequivalent methyl groups from the former diene ligand, and four methyl groups from two nonequivalent xylyl groups with hindered rotation around the N-C(arene) bond. The assignment of the olefinic protons H¹ and H² is possible from the 2D $^1\text{H}, ^1\text{H}$ -COSY NMR spectrum (Figure 1), where the resonances at 2.77 (H¹) and 1.70 ppm (H²) show a pronounced cross peak. Informative also is the presence of a weaker cross peak due to the homoallylic coupling between H² and one of the methylene protons, H³. The cis configuration around the double bond is indicated by the very small $^3J_{\text{HH}}$ (2.3 Hz) between H¹ and H². In the ^{13}C NMR spectrum (Table II) a quaternary carbon atom (δ 44.71 ppm) can be observed, as well as two doublets for the olefinic CH= groups ($\delta(\text{CH}^1)$ 43.80 ppm (d, $^1J_{\text{CH}}$ = 183.4 Hz); $\delta(\text{CH}^2)$ 28.66 ppm (d, $^1J_{\text{CH}}$ = 168.5 Hz); the assignment of these carbon atoms to the respective protons was confirmed by a 2D $^{13}\text{C}, ^1\text{H}$ -correlation NMR spectrum). The latter are found at relatively high field, indicating interaction of the double bond with the metal center.⁸ This is also suggested by the IR spectrum of 3 where a C=C vibration is visible at 1589 cm^{-1} . The presence of C-N vibrations at 1261 (s) and 1229 (vs) cm^{-1} and the absence of vibrations from CN multiple bonds demonstrate the bond order reduction of the isocyanide NC units to single C-N bonds.

The reaction of the isoprene complex 2 yields selectively one isomer, $\text{Cp}^*\text{Hf}(\text{Cl})\text{N}(\text{xy})\text{CCH}_2\text{C}(\text{Me})=\text{CHCH}=\text{CHN}(\text{xy})$ (4). The location of the methyl group, adjacent to the methylene group, is suggested by the chemical shift of the methyl protons and the strong coupling between the methyl and methylene protons observed in the 2D $^1\text{H}, ^1\text{H}$ -COSY NMR spectrum of 4. However, it proved difficult to obtain conclusive information on the stereochemistry of the product. The IR spectrum of 4 shows that two C=C double bonds are present, nonconjugated due to the conformation of the seven-membered ring: $-\text{CH}=\text{CH}-$, coordinated to the metal ($\nu_{\text{C}=\text{C}}$ = 1592 cm^{-1}), and $-\text{CH}=\text{C}(\text{Me})-$, free ($\nu_{\text{C}=\text{C}}$ = 1642 cm^{-1}). The latter vibration cannot be identified in the IR spectrum of 3, probably due to the tetrasubstitution of the double bond and the consequent low intensity of the band.

A possible route for the formation of this type of compound is shown in Scheme I. In this reaction the initial adduct 5 was not observed, but its presence is likely as intermediate adducts of this kind have either been spectroscopically identified (CO⁴) or isolated (Ph_2CO^3 , 2,6-xylyl cyanide⁹) in other reactions. Insertion of the isocyanide into a Hf-C σ -bond leading to iminoacyl 6 could then be



followed by a 1,2-hydrogen shift yielding a vinylamide derivative, 7. A similar 1,2-hydrogen shift in a Hf iminoacyl forming a vinylamide was recently reported in the reaction of $\text{Cp}_2\text{Hf}[2-(6\text{-methylpyridyl})\text{methyl}]_2$ with 2,6-xylyl isocyanide.⁹ However, in that case the conformation around the double bond is trans, with $^3J_{\text{HH}}$ = 12–13 Hz. That both the olefinic and the methylene protons in 3 stem from the diene methylene groups in the starting material was demonstrated by repeating the reaction with 1-*d*₄, the diene methylene carbons being selectively deuteriated. The ^1H NMR spectrum of 3-*d*₄ was identical with that of 3, but lacking the resonances of the olefinic and methylene protons. After the mentioned 1,2-H shift the reaction can proceed by insertion of a second isocyanide in the other Hf-C bond, forming iminoacyl 8, followed by a ring closure reaction, yielding 3. The carbenic character of transition metal and actinide acyl and iminoacyl complexes appears to be well documented by reactivity (e.g. intra-^{2b,c,10} and intermolecular¹¹ C,C coupling) and has been treated by MO calculations.¹² The ring closure observed here is equivalent to the one proposed earlier by us for the reaction of 1 with CO yielding 1,2-dimethyl-1,3-cyclopentadiene and $[\text{Cp}^*\text{Hf}(\text{O})\text{Cl}]_x$ ⁴ but is preceded by another insertion

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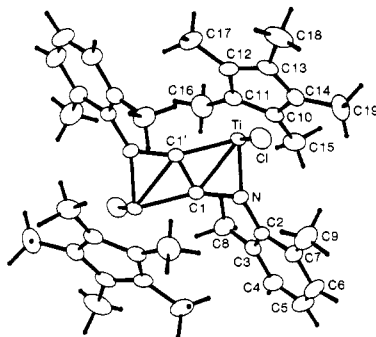
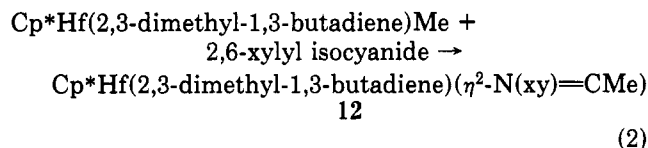


Figure 2. Molecular structure of $(\text{Cp}^*\text{TiCl})_2[\mu\text{-N}_2\text{C}_2(\text{xy})_2]$ (14).

reaction and the aforementioned 1,2-hydrogen shift. The apparent preference for the 1,2-H shift in iminoacyl **6**, in contrast to the ring closure in the corresponding acyl from the CO reaction, causes the difference in product formation between the CO and isocyanide reactions.

Reaction of Cp*Hf(2,3-dimethyl-1,3-butadiene)R (R = Me(9), Ph(10), Neopentyl (11)) with 2,6-Xylyl Isocyanide. 9 reacts with 1 mol of 2,6-xylyl isocyanide in toluene at room temperature to give a red crystalline product with stoichiometry $C_{26}H_{37}HfN$ (elemental analysis). From NMR and IR spectroscopic data (cf. Experimental Section) it can be seen that in this case a simple iminoacyl complex, $Cp^*Hf(2,3\text{-dimethyl-1,3-butadiene})(\eta^2\text{-N(xy)=CMe})$ (12) has been formed (eq 2). Se-



lective insertion of the isocyanide in the Hf-CH₃ bond has occurred, leaving the diene ligand intact. The resulting iminoacyl is η^2 -bound to Hf; the iminoacyl carbon resonance is found in the ¹³C NMR spectrum at characteristically low field (δ 269.9 ppm,¹³ IR ν_{CN} = 1550 cm⁻¹). In this case insertion of the isocyanide into the Hf-Me bond is favored above insertion into one of the Hf-diene CH₂ bonds. However, increasing the steric bulk of the Hf-bound hydrocarbyl group (e.g. by replacing the methyl by a phenyl or neopentyl group) reverses this preference: compounds **10** and **11** each again react with 2 mol of isocyanide to form products related to **3**, the Hf-Ph and Hf-CH₂CMe₃ bonds remaining intact. This can be seen from the marked downfield shifts of the hydrocarbyl α -C ¹³C NMR resonances (Table II) compared to the parent hydrocarbons. The same is observed in the spectra of **10** and **11**.² Thus the reactivity pattern of 2,6-xylyl isocyanide toward Cp*Hf(2,3-dimethyl-1,3-butadiene)R appears to be finely controlled by the steric requirements within the molecule.

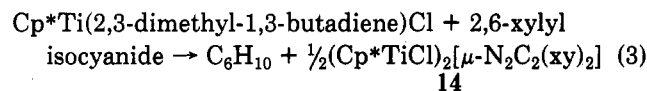
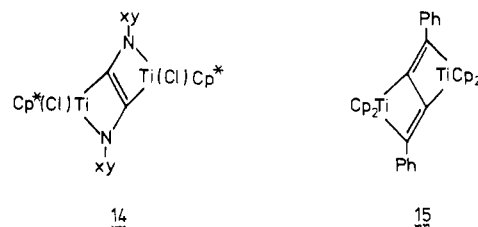
Reaction of Cp*Ti(2,3-dimethyl-1,3-butadiene)Cl (13) with 2,6-Xylyl Isocyanide. 13 reacts with 2,6-xylyl isocyanide in toluene at -30°C to give a moderately soluble green crystalline product. Elemental analysis and NMR spectroscopy indicate that the diene fragment is absent in this product and that it contains one xylyl group per Cp*Ti moiety. Production of free 2,3-dimethyl-1,3-butadiene could be observed by NMR. X-ray diffraction showed that a dimeric complex, $(\text{Cp}^*\text{TiCl})_2[\mu\text{-N}_2\text{C}_2(\text{xy})_2]$ (14), had been formed (eq 3). The molecular structure of

Table III. Interatomic Distances (Å) and Angles (deg) in (Cp*TiCl)₂[μ-N₂C₂(C₆Me₂H₃)₂] (14)^a

Ti-Cl	2.301 (1)	Ti-C(10)	2.333 (3)
Ti-C(1 ⁱ)	2.020 (3)	Ti-C(11)	2.340 (3)
Ti-C(1)	2.218 (3)	Ti-C(12)	2.365 (3)
Ti-N	1.904 (3)	Ti-C(13)	2.382 (3)
C(1 ⁱ)-C(1)	1.418 (5)	Ti-C(14)	2.329 (3)
C(1)-N	1.402 (3)	Ti-X	2.019
N-C(2)	1.415 (3)	C(10)-C(11)	1.419 (4)
C(2)-C(3)	1.404 (4)	C(11)-C(12)	1.418 (4)
C(3)-C(4)	1.385 (4)	C(12)-C(13)	1.409 (4)
C(4)-C(5)	1.373 (5)	C(13)-C(14)	1.410 (4)
C(5)-C(6)	1.366 (5)	C(14)-C(10)	1.410 (4)
C(6)-C(7)	1.396 (5)	C(10)-C(15)	1.502 (5)
C(7)-C(2)	1.410 (4)	C(11)-C(16)	1.490 (5)
C(3)-C(8)	1.491 (4)	C(12)-C(17)	1.495 (5)
C(7)-C(9)	1.493 (5)	C(13)-C(18)	1.491 (5)
Ti...Ti ⁱ	3.999 (3)	C(14)-C(19)	1.496 (5)
Cl-Ti-N	105.30 (7)	C(5)-C(6)-C(7)	121.0 (3)
Cl-Ti-C(1)	115.23 (7)	C(6)-C(7)-C(2)	118.5 (3)
Cl-Ti-C(1 ⁱ)	109.69 (9)	C(6)-C(7)-C(9)	120.4 (3)
Cl-Ti-X	114.4	C(9)-C(7)-C(2)	121.1 (3)
N-Ti-C(1)	38.8 (1)	C(14)-C(10)-C(11)	108.3 (2)
N-Ti-C(1 ⁱ)	77.4 (1)	C(11)-C(10)-C(15)	126.6 (3)
N-Ti-X	125.6	C(14)-C(10)-C(15)	124.9 (3)
C(1)-Ti-C(1 ⁱ)	38.7 (1)	C(10)-C(11)-C(12)	107.1 (2)
C(1)-Ti-X	130.4	C(10)-C(11)-C(16)	126.9 (3)
C(1 ⁱ)-Ti-X	118.7	C(12)-C(11)-C(16)	125.8 (3)
C(1 ⁱ)-C(1)-N	121.2 (3)	C(11)-C(12)-C(13)	108.6 (2)
C(1)-N-C(2)	122.3 (2)	C(11)-C(12)-C(17)	125.5 (3)
N-C(2)-C(3)	122.4 (2)	C(13)-C(12)-C(17)	125.7 (3)
N-C(2)-C(7)	117.4 (2)	C(12)-C(13)-C(14)	107.8 (2)
C(3)-C(2)-C(7)	120.1 (2)	C(12)-C(13)-C(18)	126.3 (3)
C(2)-C(3)-C(4)	118.8 (3)	C(14)-C(13)-C(18)	125.7 (3)
C(2)-C(3)-C(8)	122.8 (2)	C(13)-C(14)-C(10)	108.1 (2)
C(8)-C(3)-C(4)	118.5 (3)	C(13)-C(14)-C(19)	126.4 (3)
C(3)-C(4)-C(5)	121.2 (3)	C(10)-C(14)-C(19)	125.4 (3)
C(4)-C(5)-C(6)	120.2 (3)		

^a Estimated standard deviations are given in parentheses. Symmetry code (i): \bar{x} , \bar{y} , \bar{z} . X is the center of gravity of the five-membered ring C(10)–C(14).

14 is shown in Figure 2; bond lengths and angles are given in Table III. The structure demonstrates that a C.C



coupling of two isocyanide carbon atoms has taken place between two unsaturated metal centers, formed by elimination of the diene ligands. C,C coupling of isocyanide carbons without prior insertion into a metal-carbon bond is comparatively rare. Notable cases are found in the reduction of $[M(CNR)_6X]^+$ ($M = Mo, W$; $R = \text{alkyl}$; $X = \text{halide}$) with Zn in protic solvents, which yields the (*N,N'*-dialkylamino)acetylene complexes $[M(CNR)_4(CNHR)_2X]^+$ ^{14a,b} and in reactions of metal-metal bound dimeric complexes $M_2Cl_6(SMe_2)_3$ ($M = Nb, Ta$) with alkyl isocyanides.^{14c,d} The bridging unit in 14 shows considerable resemblance to that in the dimerization product of

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(14) (a) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617. (b) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *Ibid.* **1982**, *104*, 1263. (c) Cotton, F. A.; Roth, W. J. *Ibid.* **1983**, *105*, 3734. (d) Cotton, F. A.; Duraj, A.; Roth, W. J. *Ibid.* **1984**, *106*, 6987.

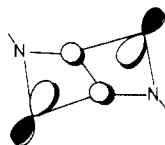
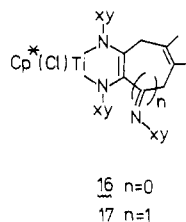


Figure 3. Representation of Ti-C(1) π -interaction in 14.

$\text{Cp}_2\text{TiC}\equiv\text{CPh}$, $(\text{Cp}_2\text{Ti})_2(\text{PhC}_4\text{Ph})$ (15),¹⁵ with one double bond less due to the extra electron on N. Just as it is possible to see 15 as a complex of 1,4-diphenylbutadiyne,¹⁵ 14 can be considered as a complex of the heterocumulene $(\text{xy})\text{N}=\text{C}=\text{C}=\text{N}(\text{xy})$.

The structure of 14 is built around an approximately planar raftlike $\text{Ti}_2\text{N}_2\text{C}_2$ framework (the dihedral angle between the Ti, N, C(1) and Ti, C(1), C(1') planes is 173.5° (2°), with the Cp^* and Cl ligands in a trans arrangement. The xyllyl α -carbons lie 0.145 (3) Å from the least-squares plane through the $\text{Ti}_2\text{N}_2\text{C}_2$ fragment, with the aromatic rings lying roughly in the diagonal plane between the Cp^* rings, the dihedral angle between the aromatic ring and the Cp^* ring being 26° . The Ti-C(1') distance (2.020 (3) Å) is relatively short for a Ti-C σ -bond.¹⁶ The Ti-C(1) distance (2.218 (3) Å) is 0.2 Å longer but still shorter than the Ti-C σ -bonds in, e.g., Cp_2TiPh_2 (2.272 (14) Å).¹⁷ EHMO calculations on the bent CpZrCl fragment² have shown that the bent CpMCl moiety has an empty orbital (NLUMO in CpZrCl) of correct symmetry and composition to effect π -interaction between Ti and C(1) perpendicular to the $\text{Ti}_2\text{N}_2\text{C}_2$ plane in 14 (Figure 3). This interaction effectively removes electron density from the C(1)-C(1') π -bond and can be related to the relatively long C=C distance of 1.418 (5) Å.

Compound 14 was isolated in 47% yield and is clearly the major product in this reaction. However, in the mother liquor two pentane-soluble side products are present, which can, through repeated recrystallization, be separated well enough to allow spectroscopic identification. NMR spectroscopy shows that both compounds still contain the former diene ligand, with different Cp^* to xyllyl ratios: 1:2 (16, $n = 0$, red crystals) and 1:3 (17, $n = 1$, orange-brown needles). On the basis of ^1H and ^{13}C NMR spectroscopy,



both products are identified as enediamide complexes, comparable to the compounds produced in the 2,6-xyllyl isocyanide reactions of $\text{Ta}(\text{CH}_2\text{Ph})_2(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_3$ ¹⁸ and $\text{Ti}(\text{CH}_2\text{Ph})_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2$,^{7c} respectively. 16 contains a mirror plane, showing resonances for two identical methylene ($\delta(\text{CH}_2)$ 2.68 ppm (br s); $\delta(\text{CH}_2)$ 44.76 ppm (t, 130 Hz)) and methyl ($\delta(\text{CH}_3)$ 1.24 ppm (s); $\delta(\text{CH}_3)$ 13.24 ppm (q, 127 Hz)) groups from the former diene ligand as

(15) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376.

(16) Generally, Ti(IV)-C σ bond distances lie in the region 2.10–2.20 Å, for example, see: Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. Tebbe, F. N.; Harlow, R. L. *Ibid.* **1980**, *102*, 6149. Dawoodi, Z.; Green, M. L. H.; Mtetawa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629.

(17) Kockman, V.; Rucklidge, J. C.; O'Brien, R. J.; Santo, W. *J. Chem. Soc., Chem. Commun.* **1971**, 1340.

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well as methyl resonances of two identical xyllyl groups with hindered rotation (on the NMR time scale) around the N-C(arene) bond. In contrast, the structure of 17 is asymmetric ($\delta(\text{CH}_2)$ 2.60, 2.74 ppm (d, $^2J_{\text{HH}} = 15.5$ Hz) and 3.23, 3.52 ppm (d, $^2J_{\text{HH}} = 17.0$ Hz); $\delta(\text{CH}_2)$ 42.30 ppm (t, 128.5 Hz) and 44.77 ppm (t, 130.0 Hz)), with two nonidentical xyllyl groups with hindered rotation around the N-C(arene) bond as well as one freely rotating xyllyl group.

Concluding Remarks

The reactivity of 14-electron diene complexes of Ti and Hf toward 2,6-xyllyl isocyanide demonstrates that electronic unsaturation in early-transition-metal complexes can induce the formation of unusual and quite complex organometallic products. The relatively weak Ti-diene bond in 13 allows for the in situ generation of unsaturated 10-electron Cp^*TiCl fragments, capable of performing the observed unorthodox C,C coupling of two isocyanide molecules. From the product formation described above, it is clear that the Ti complex 13 is less inclined to react as a σ^2, π -metallacyclopentene complex than its Hf counterpart 1. A comparable difference in reactivity between 1 and 13 was found in their reactions with acetylene.⁵ A decrease in the σ^2, π -metallacyclopentene character in $\text{Cp}^*\text{M}(2,3\text{-dimethyl-1,3-butadiene})\text{Cl}$ upon going from Hf to Ti can be anticipated from the absolute value of the geminal coupling constant of the diene methylene protons, which decreases from 11.0 Hz for $\text{M} = \text{Hf}$ to 8.7 Hz for $\text{M} = \text{Ti}$.² It is remarkable that when, eventually, insertion of isocyanide into the Ti-diene bond does take place, a different reaction path is chosen, as the Ti-complexes do not exhibit the 1,2-hydrogen shift found in Hf complexes like 3.

Experimental Section

General Considerations. All manipulations were carried out by using Schlenk and glovebox techniques under nitrogen. All solvents were distilled from Na/K alloy under nitrogen before use. Compounds 1, 2, 9–11, and 13 were prepared according to ref 2. 1- d_4 was prepared analogously to 1, using 1,1,4,4-tetra-deuterio-2,3-dimethyl-1,3-butadiene, synthesized from 2,3-dimethyl-1,3-butadiene according to ref 19 and 20. 2,6-Xyllyl isocyanide was prepared as in ref 21. ^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-200 or a Varian VXR-300 spectrometer. IR spectra were recorded from Nujol mulls between KBr disks on a Pye-Unicam SP3-300 spectrophotometer. Elemental analyses were performed at the microanalytical department of the chemical laboratories, Groningen University.

$\text{Cp}^*\text{Hf}(\text{Cl})\text{N}(\text{xy})\text{CCH}_2\text{C}(\text{Me})\text{CH}=\text{CHN}(\text{xy})$ (3) and Related Compounds. A solution of 2,6-xyllyl isocyanide (0.820 g, 6.16 mmol) in 10 mL of toluene was added dropwise in 10 min to a solution of 1 (1.35 g, 3.13 mmol) in 5 mL of toluene at room temperature, during which the orange solution changed to brown-red. After the solution was stirred at room temperature for 16 h, the solvent was pumped off from the pale red solution. The residue was washed with pentane to yield an off-white solid. Recrystallization from hot benzene gave analytically pure 3 (0.960 g, 1.38 mmol, 45%). Anal. Calcd for $\text{HfC}_{34}\text{H}_{43}\text{ClN}_2$: C, 58.87; H, 6.25; Hf, 25.73; mol wt (cryoscopy in benzene), 694. Found: C, 58.86; H, 6.32; Hf, 25.27; mol wt, 679. Decomposition temperature: 239 $^\circ\text{C}$ (DTA). 4 was prepared similarly from the isoprene complex 2. Similar procedures were also used to prepare the phenyl and neopentyl derivatives starting from 10 and 11. Anal. Calcd for the neopentyl derivative, $\text{HfC}_{39}\text{H}_{54}\text{N}_2$: C, 64.17;

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(21) Shingaki, T.; Takebayashi, M. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 617.

Table IV. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2) for the Non-Hydrogen Atoms in $(\text{Cp}^*\text{TiCl})_2[\mu\text{-N}_2\text{C}_2(\text{C}_6\text{Me}_2\text{H}_3)_2]$ (14)

atom	x	y	z	B_{eq}^a
Ti	0.14708 (4)	0.06551 (2)	0.07474 (6)	1.64 (1)
Cl	0.20495 (7)	0.09553 (4)	0.34924 (8)	2.94 (2)
C(1)	0.0350 (2)	-0.0309 (1)	0.0057 (3)	1.79 (7)
N	0.1688 (2)	-0.0316 (1)	0.0738 (3)	2.01 (6)
C(2)	0.2415 (2)	-0.0920 (1)	0.0797 (3)	2.18 (7)
C(3)	0.2233 (3)	-0.1342 (1)	-0.0589 (4)	2.42 (8)
C(4)	0.2953 (3)	-0.1937 (2)	-0.0411 (5)	3.24 (10)
C(5)	0.3867 (3)	-0.2103 (2)	-0.1071 (5)	3.92 (11)
C(6)	0.4095 (3)	-0.1676 (2)	0.2402 (5)	3.74 (10)
C(7)	0.3373 (3)	-0.1080 (2)	0.2310 (4)	2.90 (9)
C(8)	0.1319 (3)	-0.1168 (2)	-0.2260 (4)	3.17 (10)
C(9)	0.3606 (4)	-0.0630 (2)	0.3792 (5)	4.32 (12)
C(10)	0.2551 (3)	0.0877 (1)	-0.1104 (3)	2.27 (8)
C(11)	0.1258 (3)	0.1077 (1)	-0.1883 (3)	2.31 (8)
C(12)	0.1026 (3)	0.1639 (1)	-0.0972 (4)	2.66 (8)
C(13)	0.2157 (3)	0.1782 (1)	0.0350 (4)	2.69 (9)
C(14)	0.3089 (3)	0.1299 (1)	0.0293 (3)	2.44 (8)
C(15)	0.3273 (4)	0.0350 (2)	-0.1718 (5)	3.55 (11)
C(16)	0.0341 (4)	0.0794 (2)	-0.3445 (4)	3.84 (11)
C(17)	-0.0176 (4)	0.2053 (2)	-0.1435 (6)	4.43 (13)
C(18)	0.2365 (5)	0.2367 (2)	0.1536 (6)	4.49 (15)
C(19)	0.4427 (3)	0.1247 (2)	0.1478 (5)	4.04 (12)

$$^a B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

H, 7.46; Hf, 24.45. Found: C, 64.60; H, 7.69; Hf, 24.50. The phenyl derivative was spectroscopically characterized without recrystallization (Table II).

Cp*Hf(2,3-dimethyl-1,3-butadiene)($\eta^2\text{-Nxy=CMe}$) (12). A solution of 2,6-xylyl isocyanide (0.258 g, 1.97 mmol) in 5 mL of toluene was added dropwise in 10 min to a solution of 9 (0.81 g, 1.97 mmol) in 5 mL of toluene at 0 °C, during which the yellow solution changed to deep red. After the solution was stirred for 4 h at room temperature, the solvent was pumped off. The red solid was recrystallized from diethyl ether to yield analytically pure 12 (0.500 g, 0.92 mmol, 47%): ^1H NMR (200 MHz, C_6D_6 , 20 °C) δ 6.95 (ps s, 3 H, xy-Ar), 2.07 (s, 3 H, $\text{C}(\text{CH}_3)=\text{N}$), 2.04 (s, 15 H, Cp*), 2.01 (br s, 6 H, $\text{CH}_2=\text{C}(\text{CH}_3)$), 1.96 (s, 6 H, xy-Me), \approx 2.0 (overlapped by other resonances, syn $=\text{CH}_2$), -0.23 (d, 10.2 Hz, 2 H, anti $=\text{CH}_2$); ^{13}C NMR (50.3 MHz, C_6D_6 , 20 °C) δ 11.8 (q, 126 Hz, Cp*-Me), 23.4 (q, 126 Hz, $\text{C}(\text{CH}_3)=\text{CH}_2$), 24.7 (q, 126 Hz, $\text{C}(\text{CH}_3)=\text{N}$), 58.1 (dd, 134, 145 Hz, $=\text{CH}_2$), 116.3 (s, C_5Me_5), 119.7 (s, $=\text{CMe}$), 262.9 (s, $\text{CMe}=\text{N}$), xy-resonances at 19.9 (q, 127 Hz), 125.4 (d, 160 Hz), 128.7 (d, 160 Hz), 129.6 (s), 142.6 (s); IR $\nu(\text{C}=\text{N}) = 1550 \text{ cm}^{-1}$. Anal. Calcd for $\text{HfC}_{26}\text{H}_{37}\text{N}$: C, 57.61; H, 6.88; Hf, 32.93. Found: C, 57.30; H, 6.87; Hf, 33.15.

Reaction of Cp*Ti(2,3-dimethyl-1,3-butadiene)Cl (13) with 2,6-Xylyl Isocyanide. Toluene (20 mL) was vacuum transferred onto a mixture of solid 13 (0.395 g, 1.31 mmol) and 2,6-xylyl isocyanide (0.314 g, 2.39 mmol). The mixture was thawed out and stirred for 20 min at -30 °C, giving a brown solution with green microcrystalline material. The solvent was removed in vacuo at room temperature and the green residue extracted with 35 mL of pentane. The remaining solid was recrystallized by diffusion of pentane into a toluene solution, yielding 0.216 g (0.31 mmol, 47%) of analytically pure 14: ^1H NMR (300 MHz, C_6D_6 , 23 °C) δ 7.0-6.9 (m, 6 H, xy-Ar), 2.58 (s, 6 H, xy-Me), 2.26 (s, 6 H, xy-Me), 1.74 (s, 30 H, Cp*); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, C_6D_6 , 23 °C) δ 11.78 (Cp*-Me), 22.62, 22.88 (xy-Me), 125.83 (C_5Me_5), 125.20, 128.80, 129.21 (xy-CH), 132.27, 137.38, 146.85 (xy-C), 185.94 ($=\text{CN}$); IR 3050 (vw), 1460 (vs), 1426 (sh), 1372 (m), 1294 (s), 1278 (s), 1246 (mw), 1152 (vw), 1115 (w), 1060 (w), 778 (sh), 770 (s), 604 (vw), 550 (vw), 512 (vs), 495 (s), 416 (m), 383 (m) cm^{-1} . Anal. Calcd for $\text{Ti}_2\text{C}_{38}\text{H}_{48}\text{Cl}_2\text{N}_2$: C, 65.25; H, 6.92; Cl, 10.14. Found: C, 65.55; H, 7.01; Cl, 10.34.

From the pentane extract 16 and 17 could be isolated (70-100 mg each) after repeated recrystallization from pentane in sufficient purity to allow NMR spectroscopic characterization.

16: ^1H NMR (300 MHz, C_6D_6 , 23 °C) δ 6.97 (ps s, 6 H, xy-Ar), 2.68 (br s, 4 H, CH_2), 2.66 (s, 6 H, xy-Me), 2.26 (s, 6 H, xy-Me), 1.74 (s, 15 H, Cp*), 1.24 (s, 6 H, $=\text{C}(\text{CH}_3)$); ^{13}C NMR (75.4 MHz, C_6D_6 , 23 °C) δ 11.51 (q, 127 Hz, Cp*-Me), 13.24 (q, 127 Hz, $=\text{C}(\text{CH}_3)$), 20.66 (q, 124 Hz, xy-Me), 22.78 (q, 128 Hz, xy-Me),

44.76 (t, 130 Hz, $-\text{CH}_2-$), 125.55 (d, 159 Hz, xy-CH), 126.86 (s, C_5Me_5), 129.13 (d, 158 Hz, xy-CH), 129.61 (s, C), 131.30 (s, xy-C), 136.05 (s, xy-C), 147.61 (s, xy-C). Assignment of resonances in the region of 126-130 ppm is difficult due to extensive overlap.

17: ^1H NMR (300 MHz, C_6D_6 , 23 °C) δ 7.0-6.6 (m, 9 H, xy-Ar), 3.52, 3.23 (each d, 17.0 Hz, 1 H, $-\text{CHH}-$), 2.60, 2.74 (each d, 15.5 Hz, 1 H, $-\text{CHH}-$), 2.27, 2.41, 2.46, 2.65 (each s, 3 H, xy-Me), 2.00 (s, 6 H, xy-Me), 1.80 (s, 15 H, Cp*), 1.39, 1.02 (each s, 3 H, $=\text{C}(\text{CH}_3)$); ^{13}C NMR (75.4 MHz, C_6D_6 , 23 °C) δ 11.77 (q, 126.8 Hz, Cp*-Me), 13.11 (q, 125.4 Hz, $=\text{C}(\text{CH}_3)$), 13.55 (q, 125.3 Hz, $=\text{C}(\text{CH}_3)$), 18.98, 19.64, 19.92, 20.10, 20.20 (each q, 125 Hz, xy-Me), 42.30 (t, 128.5 Hz, $-\text{CH}_2-$), 44.77 (t, 130 Hz, $-\text{CH}_2-$). The assignment of resonances in the downfield region is difficult due to the complexity and extensive overlap in this part of the spectrum.

X-ray Structure Determination of 14. Crystal Data and Data Collection. A suitable crystal of 14 ($0.29 \times 0.18 \times 0.45$ mm), obtained by slow diffusion of pentane into a toluene solution, was mounted in epoxy resin. 14 crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.111$ (8) \AA , $b = 19.435$ (17) \AA , $c = 8.592$ (4) \AA , $\beta = 109.68$ (5)°, $Z = 2$, $d_{\text{calc}} = 1.33 \text{ g cm}^{-3}$, and $\mu(\text{Mo K}\alpha) = 6.57 \text{ cm}^{-1}$. The diffracted intensities ($+h, +k, \pm l$) for $3.5 < 2\theta < 50^\circ$ were measured in a stream of dinitrogen of 170 K with a Syntex P2, diffractometer, using graphite-monochromated Mo K α radiation and the ω - 2θ scan mode with a variable 2θ scan rate of 2.5 - $29.3^\circ \text{ min}^{-1}$. A 96-step profile was recorded for each reflection, and intensities were calculated according to ref 22 and 23. Of the 3089 independent reflections measured, excluding those systematically absent, 2462 had $I > 3\sigma(I)$ and were regarded as observed. Monitoring two reference reflections at regular intervals (after every 23 reflections measured) showed no decay of the crystal. Intensity data were corrected for Lorentz and polarization effects, but not for absorption. Unit cell parameters were obtained from diffractometer setting angles for 15 reflections.

Structure Determination and Refinement. The coordinates of the Ti and Cl atoms were obtained from the Patterson function and those of the C and N atoms from a subsequent electron-density map. Full-matrix least-squares refinement of positional and isotropic thermal parameters and, subsequently, of anisotropic thermal parameters yielded $R = 0.060$ (199 parameters). Inclusion of positional and isotropic thermal parameters for the hydrogen atoms, located from a difference map, gave a final $R = 0.040$ and $R_w = 0.046$ for 295 parameters and 2462 reflections. Atomic scattering factors were taken from ref 24, and the F_o values were weighted according to $w = [\sigma^2(F_o) + 0.00075F_o^2]^{-1}$. A final difference map showed a maximum residual density of 0.52 e \AA^{-3} . Fractional coordinates for the non-hydrogen atoms are given in Table IV. The computer programs used are described in ref 25.

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Registry No. 1, 106499-70-1; 2, 106499-77-8; 3, 118376-45-7; 3 (phenyl deriv.), 118376-46-8; 3 (neopentyl deriv.), 118376-47-9; 4, 118398-05-3; 9, 106564-97-0; 10, 106499-73-4; 11, 106499-72-3; 12, 118376-48-0; 13, 106457-12-9; 14, 118376-51-5; 16, 118376-49-1; 17, 118376-50-4; 2,6-xylyl isocyanide, 2769-71-3.

Supplementary Material Available: A 2D $^{13}\text{C}, ^1\text{H}$ -correlated NMR spectrum of 3 and a 2D $^1\text{H}, ^1\text{H}$ -COSY NMR spectrum of 4 and tables of anisotropic thermal parameters for the non-hydrogen atoms, thermal and positional parameters, and bond distances for the hydrogen atoms for 14 (5 pages); a listing of observed and calculated structure factors for 14 (15 pages). Ordering information is given on any current masthead page.

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